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Preliminary communication

A NOVEL SYNTHESIS AND X-RAY STRUCTURE OF A NEW ARYLDIAZENE COMPLEX: *trans*-(PHENYLACETYLIDE)BIS(TRIPHENYLPHOSPHINE)(*p*-FLUOROPHENYLDIAZENE)PLATINUM(II) TETRAFLUOROBORATE

U. CROATTO, L. TONIOLO*
Istituto di Chimica Generale ed Inorganica e di Chimica Inorganica Industriale, Università, Padova (Italy)
A. IMMIRZI
Istituto di Chimica delle Macromolecole del C.N.R., Milano (Italy)
and G. BOMBIERI
Centro di Chimica e Tecnologia dei Radioelementi-C.N.R., Padova (Italy)

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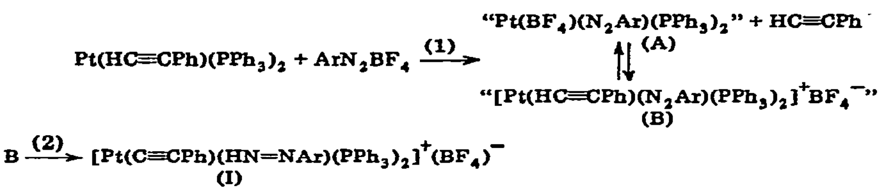
Summary

The title compound $[Pt(CCPh)(HNNC_6H_4F\text{-}p)(PPh_3)_2](BF_4)$ has been synthesized from $Pt(HC{\equiv}CPh)(PPh_3)_2$ and $p\text{-}FC_6H_4N_2BF_4$, and a mechanism for its formation is proposed; X-ray diffraction studies show that the acetylide ligand is σ-bonded and that the P—C≡C—C system is essentially linear, while the diazene ligand has a *trans* configuration around the N=N bond, and the hydrogen-bearing nitrogen atom is coordinated to the platinum.

The chemistry and mode of coordination of aryldiazene transition metal complexes are receiving increasing interest [1, 2]. Until now they have been synthesized by insertion of an aryldiazonium cation into a M—H bond, or by protonation at the coordinated nitrogen of an aryldiazo complex [1].

The new title compound I has now been synthesized in a novel way from $Pt(HC{\equiv}CC_6H_5)(PPh_3)_2$ and $p\text{-}FC_6H_4N_2BF_4$ in benzene—ethanol at room temperature. I probably forms in two steps: (1) formation of a platinum(II) complex containing the reduced $ArN{=}N^-$ ligand, as noted in the synthesis of "$Pt(BF_4)(N_2Ar)(PPh_3)_2$" (A) [3]; (2) formation of the Pt—C≡CPh σ-bond, acetylenic hydrogen transfer to the diazo moiety, and *trans*-rearrangement to yield I. This suggestion is supported by the fact that treatment of separately prepared A with the alkyne yields I. The second step would be promoted by activation of the acetylenic C—H bond by the metal atom (Scheme 1).



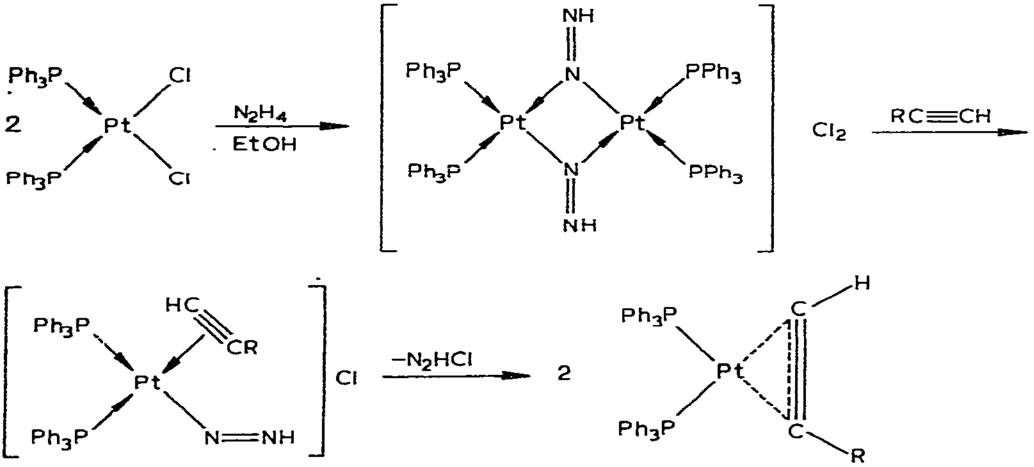
$$\begin{array}{ll} \mathrm{Pt(HC{\equiv}CPh)(PPh_3)_2 + ArN_2BF_4 \xrightarrow{(1)}} & \text{“}\mathrm{Pt(BF_4)(N_2Ar)(PPh_3)_2}\text{”} + \mathrm{HC{\equiv}CPh} \\ & \quad \updownarrow \text{(A)} \\ & \text{“}\mathrm{[Pt(HC{\equiv}CPh)(N_2Ar)(PPh_3)_2]^+BF_4^-}\text{”} \\ & \quad \text{(B)} \end{array}$$

$$\mathrm{B \xrightarrow{(2)} [Pt(C{\equiv}CPh)(HN{=}NAr)(PPh_3)_2]^+(BF_4)^-}$$

(I)

SCHEME 1

The formation of I is related to the reverse of the synthesis of the starting complex $Pt(PPh_3)_2(PhC{\equiv}CH)$ from *cis*-$Pt(PPh_3)_2Cl_2$ and phenylacetylene in the presence of hydrazine. However, in this synthesis the $H{-}N{=}N^-$ species, unlike the related $ArN{=}N^-$ entity which appears in Scheme 1, decomposes to molecular nitrogen and no C—H bond breaking occurs [4], as shown in Scheme 2.



SCHEME 2

The IR spectrum of I shows $\nu(C{\equiv}C)$ at 2124 cm^{-1} in agreement with data for other phenylacetylideplatinum(II) complexes [5]. There are several bands in the 1600-1400 cm^{-1} region, where (N=N) usually occurs [2], but exact assignment by ^{15}N-substitution has not been carried out. The ^1H NMR spectrum in $CDCl_3$ shows the nitrogen-bonded proton at τ −3.5 ppm, indicating its acid character [1].

Crystal data $[Pt(CCPh)(HNNC_6H_4F)(PPh_3)_2]BF_4$. Yellow prismatic crystals. Orthorhombic $P2_12_12_1$ a 25.638(3), b 16.250(2), c 13.050(2), $Z = 4$. Present R value 0.09. 2852 independent reflections collected between θ 3° and 25° using graphite-monochromated Mo-K_α radiation (λ 0.7107 Å) on a Philips Pw-1100 automated diffractometer.

The complex is square planar with the two triphenylphosphine ligands in *trans* relation. Figure 1 shows a view of the cation unit orthogonal to the coordination plane, together with some relevant bond lengths. The $C_6H_5C{\equiv}C$ ligand is σ-bonded to the metal through the C(1) carbon atom and the Pt—C≡C—C system is essentially linear: the angles on C(1) and C(2) are 178° and 172°, respectively. It is noteworthy that in $PtCl(C{\equiv}CPh)(PPhEt_2)_2$ the corresponding

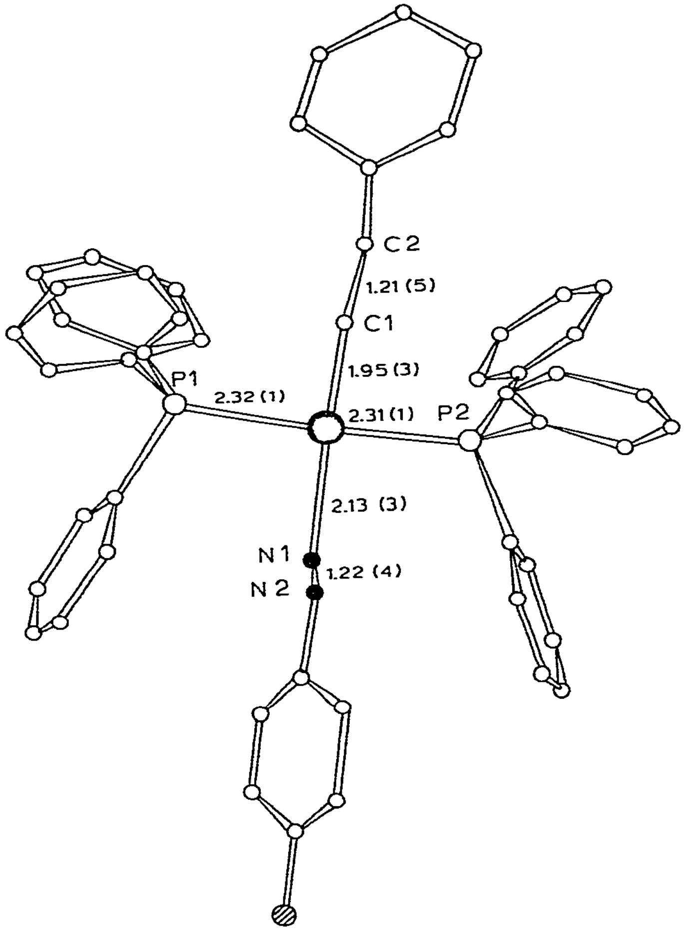


Fig. 1. View of the cation $[Pt(CCPh)(HNNC_6H_4F)(PPh_3)_2]^+$ orthogonal to the coordination plane.

system is bent (162°) at the carbon atom bonded to the metal [6]. The $HN{=}N{-}C_6H_4F$ ligand has the *trans* configuration with respect to the N(1)—N(2) bond. The Pt—N(1) bond length 2.13(3) Å is significantly influenced by the *trans* C(1) atom, and is the same as that, viz. 1.973(7) Å, in $[PtCl(HN{=}NC_6H_4F)(PEt_3)_2](ClO_4)$ [2], where the chlorine exerts little *trans* influence [7]. The N(1)—N(2) bond length of 1.22(4) Å confirms the double bond character between N(1) and N(2), and agrees with that in $[PtCl(HN{=}NC_6H_4F)(PEt_3)_2](ClO_4)$ [2].

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